

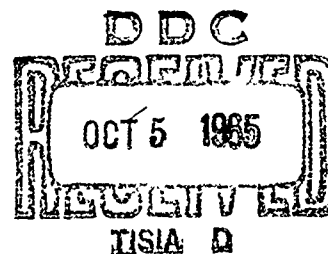
MINISTRY OF AVIATION

DIRECTORATE OF MATERIALS AND STRUCTURES RESEARCH AND DEVELOPMENT

CAGE-LIKE SILICON COMPOUNDS

J. H. Bishop AND R. A. Shaw
(BIRKBECK COLLEGE)

JULY 1965



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FOREWORD

This report was prepared by J. H. Bishop and R. A. Shaw of Birkbeck College for the Directorate of Materials and Structures Research and Development, Ministry of Aviation, under Research Agreement No. PD/46/01.

The work was planned, progressed and administered by Mat. 9 under the direction of A.D.Mat. (N.M.), Ministry of Aviation.

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SUMMARY

The factors influencing the formation of octaisopropyloctasilsesquioxane have been investigated. This compound can be brominated by means of N-bromosuccinimide. Chemical evidence and ^1H n.m.r. spectroscopy show that bromination occurs in the α -position of the isopropyl groups. Thin-layer chromatography provided a means of separating and identifying the individual components in brominated octaisopropyl T_8 materials and column chromatography was used to isolate $(\text{C}_3\text{H}_7\text{SiC}_{1.5})_8$, $(\text{C}_3\text{H}_6\text{Br})(\text{C}_3\text{H}_7)_7(\text{SiO}_{1.5})_8$, $(\text{C}_3\text{H}_6\text{Br})_2(\text{C}_3\text{H}_7)_6(\text{SiO}_{1.5})_8$ in a substitutionally pure, and $(\text{C}_3\text{H}_6\text{Br})_3(\text{C}_3\text{H}_7)_5(\text{SiO}_{1.5})_8$ in a slightly impure state from these. Some chemical reactions of the brominated derivatives and several investigations into the possibility of preparing a silazane 'cage' compound are described.

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1. INTRODUCTION. In recent years varying yields of discrete oligomers $(\text{RSiO}_{1.5})_n$ (where $n = 4, 6, 8, \dots$, $R = \text{Alk or Ar}$) have been obtained by the controlled hydrolysis of trifunctional organosilicon compounds or by the pyrolysis of suitable higher polymers obtained from these.¹⁻¹¹ These oligomers consist of highly-symmetrical three-dimensional molecules built up of trifunctional siloxane units which form cage-like structures, similar to that of adamantane, and of a number of inorganic compounds, such as phosphorus pentoxide, P_4O_{10} . A number of these have been reviewed.¹²

Whilst a few tetrameric $(\text{T}_4)^{11}$ and $(\text{T}_6)^{4,6}$ compounds have been reported, the T_8 species are the best known, and the structures of some members of this group have been determined by X-ray crystallography¹³ (for nomenclature cf. refs. 5-8). Methyl and phenyl T_{10} and T_{12} compounds have been isolated and characterised,^{4,9,10} as has been a high polymer $(\text{PhSiO}_{1.5})_n$ with a ladder-like cis-syndiotactic structure.⁹

The reactions of the organic groups, R , in these compounds have been little investigated. The lack of reactivity of octaethyl T_8 , $(\text{EtSiO}_{1.5})_8$, has been noted² and the nitration and bromination of various octa-aryl T_8 compounds in all of their aryl side-chains reported.³ Up to now unsymmetrical cage-like compounds, with only some of the organic side-chains substituted, have not been described.

2. EXPERIMENTAL. Our initial investigations dealt with the preparation of alkyl silsesquioxanes. Numerous attempts at repeating the preparation of tetraisopropyl T_4 failed completely indicating that the conditions under which it was prepared (in 55% yield) by Wiberg and Simmler¹¹ must be very critical. Scott¹⁴ has pointed out the inherent strain in the cyclotrisiloxane structure, which is demonstrated, for example, by the cleavage of hexa-ethyl T_6 by methanol.⁶

Attention was, therefore, turned to the preparation of octaisopropyl T_8 , a stable compound with a known structure.¹³

Using Olsson's method² octaisopropyl T_8 was prepared by refluxing a dilute solution of the hydrolyzate of isopropyltrichlorosilane in strong methanolic hydrogen chloride. The product is precipitated from the refluxing solution; a small amount of waxy material is also obtained on cooling. After refluxing for 3-4 days the formation of octaisopropyl T_8 practically ceased. However, if hydrogen chloride was then passed into the cooled, filtered solution until a cloudiness appeared, further octaisopropyl T_8 formed on refluxing. Repetition of this process gives octaisopropyl T_8 , accompanied by increasing proportions of waxy materials, which eventually become the sole product. Concentration of the reaction mixture by distilling off the methanol solvent does not result in the formation of further octaisopropyl T_8 . The yield of 30% (compared with the 17% obtained by Olsson) appears to be the maximum possible by this method.

The role of the hydrogen chloride is probably not only a catalyst for the formation of octaisopropyl T_8 from the isopropyl trichlorosilane hydrolysate, as for this such high concentrations of hydrogen chloride would

hardly be necessary. It probably also aids the formation of the octamer by reducing its solubility to less than its equilibrium concentration in the equilibrated reaction mixture by effectively removing methanol by solvation, thus leading to its precipitation from solution and hence further octamer formation. Loss of hydrogen chloride from the refluxing solution causes the solubility of the octaisopropyl T_8 to rise to its equilibrium concentration causing precipitation to cease. The importance of solubility factors is demonstrated by the fact that very little octaisopropyl T_8 is obtained if its solubility in the reaction mixture is increased by replacing half of the methanol by tetrahydrofuran, in which the cage compound is more soluble. Pure octaisopropyl T_8 is disrupted by methanolic hydrogen chloride in the presence of acetone, another good solvent for this compound, showing that in solution its formation and decomposition are, at least in part, reversible.

Addition of the waxy byproduct obtained in octamer preparations to a fresh reaction mixture increased the speed of formation of octaisopropyl T_8 but not its overall yield, suggesting that it did not itself contain noticeable amounts of the precursors of the cage compound. Little octaisopropyl T_8 could be obtained from the waxy byproduct itself under a variety of conditions. This confirms the views of Sprung and Guenther⁸ that the precursors of T_8 compounds under acid conditions are molecules with specific structures which can condense to a cage-like structure. Brown *et al.*¹⁰ have pointed out that considerable structural rearrangement is required to convert the cis-anti-cis siloxane structure of a cis-syndiotactic phenyl T 'ladder-like' polymer to the cis-syn-cis structure of the 'cage-like' phenyl T compounds. Base catalysis was used in that study, whilst acid catalysis was employed in the present investigation. Condensation of diphenylsilanediol gives different products under these two sets of conditions.¹⁵ It may well be that acid reaction conditions are less conducive to rearrangements leading to cage-like molecules.

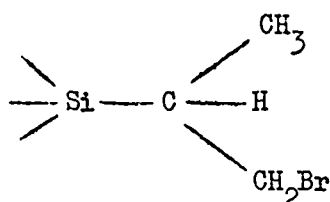
As Wiberg and Simmler¹¹ had postulated that the formation of tetra-*t*-butyl T_4 and tetraisopropyl T_4 was favoured by the bulk of the organic radical, we carefully examined the reaction mixture for cage-like molecules other than the octamer. Microscopic examination, sublimation, and chromatography failed to show their presence.

Bromination of octaisopropyl T_8 with *N*-bromosuccinimide in the presence of benzoyl peroxide and ultraviolet light was found to proceed readily. Brominated materials with any bromine content up to approximately nine bromine atoms per molecule were obtained. Increasing degrees of bromination are accompanied by steadily increasing m.p.s., and decreasing solubilities and volatilities of the materials. Their infrared spectra showed that the siloxane cage was still intact, and progressive changes with increasing bromination showed the structural similarities of the materials.

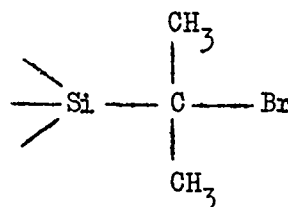
The chemical inertness of the brominated materials suggested that bromination had occurred in the α -position of the isopropyl groups as β -halogenoalkyl groups are usually very readily cleaved from silicon bonds.¹⁶

Clear evidence that the bromine atoms are substituted on the α -carbon atoms of the isopropyl groups is provided by 1H n.m.r. spectroscopy. Materials corresponding stoichiometrically to $(C_3H_6Br)(C_3H_7)_7(SiO_{1.5})_8$, $(C_3H_6Br)_2(C_3H_7)_6(SiO_{1.5})_8$ and $(C_3H_6Br)_3(C_3H_7)_5(SiO_{1.5})_8$ were examined. The n.m.r. spectrum of octaisopropyl T_8 showed a band at $\tau 8.95$ with a shoulder at 8.93 . As $C-CH_3$ is in general less shielded than $Si-CH_3$, and the same can be anticipated for $C-CH$ and $Si-CH$, little chemical shift is expected between the

methyl and methine protons of $\text{Si-CH}(\text{CH}_3)_2$, thus leading to a second order spectrum which is here insufficiently resolved. The brominated material analysing for $(\text{C}_3\text{H}_6\text{Br})_2 (\text{C}_3\text{H}_7)_7 (\text{SiO}_{1.5})_8$ gave a spectrum with bands at τ 8.98 and 8.20. The half-height band widths were approximately equal, and thus the ratio of band heights, 1:0.1, gave an approximate measure of the relative intensities. For an α -bromine atom as in structure (I) a peak at about 8.95



(I)



(II)

would be expected for 53 protons and a second peak (or rather doublet) for 2 protons. The bromine atom in ethyl bromide, $\text{CH}_3\text{CH}_2\text{Br}$, shifts the CH_2 protons 1.8 p.p.m. downfield. For a bromine atom as in structure (II) a peak of 8.95 for 49 protons and a second peak for 6 protons would be expected. The position of the second peak will be some 0.44 to lower fields (again using $\text{CH}_3\text{CH}_2\text{Br}$ for comparison). Clearly both the intensities and chemical shift favour structure (II) i.e. an α -bromoisopropyl group. The spectrum of the material analysing as $(\text{C}_3\text{H}_6\text{Br})_2 (\text{C}_3\text{H}_7)_6 (\text{SiO}_{1.5})_8$ again showed two peaks with peak heights in the ratio 1:0.36, one at τ 8.95 and the other at 8.20, so that bromination is again in the α -position. This was also the case with the material analysing as $(\text{C}_3\text{H}_6\text{Br})_3 (\text{C}_3\text{H}_7)_5 (\text{SiO}_{1.5})_8$.

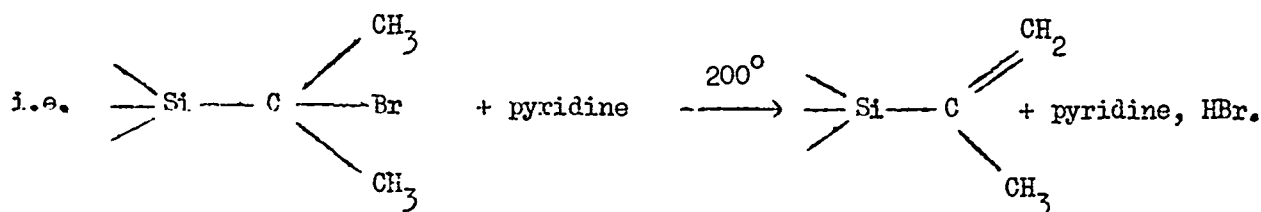
As the octaisopropyl T_8 molecule contains eight isopropyl groups it is possible for eight bromine atoms to be introduced into α -positions. It is rather unlikely that the bromination of one isopropyl group will substantially affect the reactivity of the others, because of the distance by which they are separated in a formally saturated system. One can thus expect mono-, di-, tri-, etc., bromination to occur at comparable rates and to give rise to a mixture of products of varying degrees of substitution. The situation will be further complicated by positional isomerism in di- and higher brominated products. Thus, it seems likely that the material analysing for, say, a monobromo derivative is likely to be a mixture of isomers and/or compounds of varying degrees of substitution.

We noted early on the considerable difficulties which we experienced in trying to separate and characterise individual molecular species. Melting points were uniformly high, varied with the rate of heating, occurred at comparable temperatures for products with different degrees of substitution, and were further complicated by the occurrence of polymorphism which could be observed under a polarising microscope. Furthermore, the brominated materials decomposed thermally before or during melting. Hence melting point and mixed melting point determinations were of very limited value in this field. Attempts to separate the compounds by vacuum fractional sublimation were equally unsuccessful as disproportionations and/or decomposition limited the use of this method. Thus, if octaisopropyl T_8 was sublimed, a given fraction of this taken and resublimed, this separated again into the same number of bands. Gas-liquid chromatography on the brominated materials failed, because of the thermal instability and insufficient volatility of the compounds although this method has proved successful with the methyl silsesquioxanes.⁴

Column adsorption chromatography was of only limited value as the compounds were only weakly adsorbed on the stationary phase, and eluted very rapidly under all experimental conditions tried. Thin-layer chromatography, however, indicated that materials analysing for a given degree of bromination were in fact mixtures of at least four compounds.

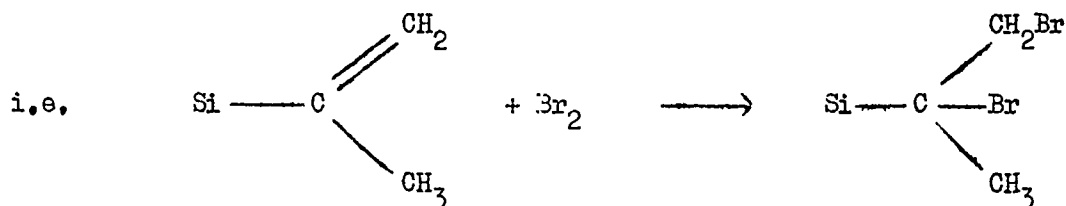
Some chemical studies were carried out with brominated products separated from non-octameric impurities and frequently corresponding analytically to a given degree of bromination. The compounds were found to be uniformly unreactive. Dehydrobromination by pyridine could be brought about at 200° but attempted halogen exchange with sodium iodide or with sodium thiocyanate even at 250° failed, although in the latter case some dehydrobromination occurred. No reaction was observed with methyl magnesium iodide in ether or tetrahydrofuran or with n-butyl magnesium bromide in ether. Under more drastic conditions such as with n-butyl lithium in refluxing n-pentane, or with methyl magnesium iodide in refluxing di-n-butyl ether reaction was observed, although the compounds could not be adequately purified and characterised. Aniline, n-butylamine and ammonia brought about dehydrobromination and failed to yield substituted amino-derivatives. Brominated products of the octaethyl T₈ compound also dehydrobrominated thermally as well as in the presence of pyridine.

The examination of the dehydrobrominated materials obtained from brominated octaisopropyl T₈ materials by ¹H n.m.r. spectroscopy showed that dehydrobromination resulted in the formation of isopropenyl groups. This was supported by their infrared spectra,



These materials exhibited resonance bands in the τ8.97, 8.12 and 4.33 regions. The band obtained in the τ8.97 region will be due to protons in the unchanged isopropyl groups present (see above), this band being absent from the spectrum of a dehydrobrominated material obtained from a material analysing as (C₃H₆BrSiO_{1.5})₈. The band obtained in the τ8.12 is due to the methyl protons present in the isopropenyl groups, deshielded by the proximity of the olefinic grouping. The band obtained in the τ4.33 region is caused by the two protons attached to the olefinic carbon atom present in each isopropenyl group.¹⁷ The relative band intensities obtained with the materials investigated were in good agreement with what one would expect from this interpretation, confirming that isopropenyl groups were indeed present. The infrared spectra showed a peak at 3065 cm.⁻¹ which increased in intensity with increasing dehydrobromination.

Bromination of one of these dehydrobrominated materials yielded a product which gave peaks at τ8.93, 8.19 and 6.40. This provided evidence that β-bromination had occurred, as the presence of a β-bromine atom as well as an α-bromine atom will further deshield the protons adjacent to the β-bromine atom so that a peak at τ6.40 is to be expected,



Bromination of another dehydrobrominated material, which had originally contained 30.6% bromine, gave a product containing 54.0% bromine, showing that β -bromination had occurred in this case also.

Thin-layer chromatography using 'silica gel G' showed that the materials obtained by the bromination of octaisopropyl T_8 were mixtures of a number of components, the relative amounts of the components with lower R_f values increasing with increasing bromine content of the sample under examination. Thus a material containing 24.9% bromine was found to consist of 4 components, R_f values 0.70, 0.80-0.86, 0.93 and 0.96. A material obtained by chlorination of octaisopropyl T_8 was less easily separated into its components.

Thin-layer chromatography proved to be the most useful means of separating and identifying the different components present in brominated octaisopropyl T_8 materials so far discovered. With its aid column chromatography, using long silica-gel columns with light petroleum (b.p. 40-60°), and mixtures of this with benzene, as the eluant, was used to separate brominated octaisopropyl T_8 materials into their components. Pure $(\text{C}_3\text{H}_7\text{SiO}_{1.5})_8$, $(\text{C}_3\text{H}_6\text{Br})(\text{C}_3\text{H}_7)_7(\text{SiO}_{1.5})_8$, and substitutionally pure $(\text{C}_3\text{H}_6\text{Br})_2(\text{C}_3\text{H}_7)_6(\text{SiO}_{1.5})_8$ were isolated, together with slightly impure $(\text{C}_3\text{H}_6\text{Br})_3(\text{C}_3\text{H}_7)_5(\text{SiO}_{1.5})_8$ and a material analysing as $(\text{C}_3\text{H}_6\text{Br})_5(\text{C}_3\text{H}_7)_3(\text{SiO}_{1.5})_8$, but shown by thin-layer chromatography to consist of at least two components. Thus bromination of octaisopropyl T_8 gives materials consisting of closely related α -bromocompounds, differing in their degree of bromination.

Although the octaisopropyl T_8 siloxane cage is cleaved by ethanolic hydrogen chloride in acetone solution, it was not cleaved or rearranged by sodium hydroxide in toluene solution although this might be expected.^{4,18,19} Cleavage of the octaisopropyl T_8 cage could also occur by reaction with organochlorosilanes at high temperatures²⁰, but again no reaction occurred.

Some attempts at preparing a silazane 'cage' compound were made. One method used was to heat methyltrimethylaminosilane, $\text{CH}_3\text{Si}(\text{NHCH}_3)_3$, prepared by the method of Tansjo²¹ in anhydrous liquid methylamine with dry methylammonium hydrochloride as catalyst (strongly acid in this medium). A wax-like solid was obtained together with a few crystals. There was insufficient product for further investigation. In another approach methyl trichlorosilane was heated in aniline in a Carius tube at 230°. It was hoped that further cleavage or rearrangement, by the aniline hydrochloride formed, of any cage-like product would be sterically prevented by the large bulk of the phenyl groups in the molecule. The complex mixture of products was partially separated into its components by fractional vacuum sublimation but no cage-like product was identified.

3. CONCLUSIONS. It was concluded that, although the possibility of the preparation of silazane 'cage' compounds existed, the extreme difficulty in isolating and identifying products rendered the present approach unsuccessful, so far.

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